RAW MATERIALS

UDC 666.1.022.8:666.122.2:666.123.22

APPLICATION OF GRANULATED RAW CONCENTRATE IN GLASS TECHNOLOGY

N. S. Krasheninnikova,[1] I. V. Frolova,[1] and V. I. Vereshchagin[1]

Translated from Steklo i Keramika, No. 5, pp. 30 – 32, May, 2004.

The possibility of using substandard materials in the form of granulated concentrates in glass technology is analyzed. It is established that using granulated concentrates in glass melting intensifies the chemical activity of batches at the stage of silicate and glass formation, which is due to the finely dispersed and defective structure of the material, close contact of the high-melting components with soda, and increased homogeneity of the batch.

One way of solving the problem of shortage of materials for the glass industry is the efficient and comprehensive use of local material resources. However, it involves certain difficulties, such as inconstant chemical compositions, the presence of various impurities, and noncompliance with state standard requirements regarding their granulometric composition.

Therefore, making a decision on replacing the traditional raw materials used in glass production, one should comprehensively research the effect of substandard materials on all stages in glass batch preparation and glass melting.

The present study analyzes the possibility of using substandard material, namely, kaolinized sand from the Tuganskoe deposit (Tomsk Region) and natural soda from the Altaiskoe deposit (Altai Region).

All the studies were comparative, involving a parallel investigation of local natural materials and the traditional materials used for glass melting, namely, Tashlinskoe sand (Ul'yanovsk region) and synthesized soda ash (Sterlitamak).

[1] Tomsk Polytechnical University, Tomsk, Russia.

The results of the study demonstrated that the mineralogical composition of Tuganskoe sand includes 98% quartz minerals and the rest feldspar, mica, and titanium compounds. Furthermore, there are single grains of zircon, tourmaline, pyroxene, andalusite, graphite, and vegetable fragments. The chemical compositions of the raw materials are listed in Tables 1 and 2.

Tuganskoe sand meets the requirements of GOST 22551–77 imposed on siliceous materials of grade VS-050-2. The presence of titanium oxide, which is a colorant impurity, may modify the color of glass.

Tuganskoe sand is classified as finely dispersed, since it contains 97% particles of size below 0.3 mm, of which up to 15% are particles of size less than 0.10 mm. In contrast, Tashlinskoe sand has 90% particles of size from 0.16 to 0.50 mm. The bulk density of Tuganskoe sand is 1339 kg/m^3 and that of Tashlinskoe sand is 1500 kg/m^3.

Along with the chemical and granulometric compositions, important parameters of glass sands are grain shape and presence of defects in grains. Electron-microscope study indicates that Tuganskoe sand has mainly grains of an angu-

TABLE 1

Material	Mass content, %						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	calcination loss
Sand:							
Tuganskoe	98.15	0.67	0.09	0.07	0.02	0.06	0.94
Tashlinskoe	99.10	0.27	0.10	0.07	0.05	–	0.41
Tuganskoe kaolin	59.32	25.50	2.38	0.70	0.50	1.34	10.26

lar fragmentary shape with a rough surface and defects in the form of microcracks and bubbles. Tashlinskoe sand contains up to 20% rounded grains with a relatively smooth surface, the rest being grains with an angular irregular configuration.

The raw soda from the Mikhailovskoe deposit contains (wt.%): 27.49 Na_2CO_3, 5.30 Na_2SO_4, 2.11 NaCl, 62.70 H_2O, and 2.40 insoluble residue.

The main defect of this raw soda is the presence of more than 60% moisture. Below we describe the results of studying natural crystalline soda produced by drying raw soda at a temperature of 350°C and subsequent milling in an disintegrator.

Natural crystalline soda differs from synthesized soda in its chemical compositions, as is has a lower content of the main component Na_2CO_3 and higher content of impurities, of which SiO_2 and Al_2O_3 are glass-forming agents and F_2O_3 is a colorant agent. Furthermore, natural soda has a relatively high content of Na_2SO_4, which is a source not only of sodium oxide but also of sulfur oxide, which is required for refining the glass melt. However, one should remember the need to simultaneously introduce reducing agents in the course of batch preparation and to take into account the negative effect of sodium sulfate on the refractory parts of the glass-melting furnace.

The granulometric composition of natural soda meets the state standard requirements, according to which the average size of soda particle has to correlate with the size of sand grains [1]. Natural soda virtually does not contain dustlike particles (less than 0.1 mm), whose quantity in synthesized soda is 18%.

Electron microscope study indicates that natural soda is represented by individual hexagonal and rod-shaped crystals. The synthesized soda contains a large quantity of loosely bound conglomerates consisting of hexagonal and round crystals with a clearly expressed pseudomorphized surface. Such conglomerates are easily destroyed in screening and form a large number of particles of size below 0.16 mm.

It is known that the size and shape of soda particles to a large extent depend on its phase composition. It is established that the diffraction pattern of natural soda, apart from reflection maxima corresponding to Na_2CO_3 and $Na_2CO_3 \cdot H_2O$, exhibit reflection maxima corresponding to $NaHCO_3$ (the product of thermal decomposition of trona) and Na_2SO_4.

Thus, the noncompliance of the properties of the local raw materials with the standard requirements on these materials primarily involving a decreased content of the main component and an increased content of colorant impurities suggests that they can be used only for a partial replacement of traditional materials in the technology of tinted glasses.

Analysis of the published data and the practice of glass production indicate that the application of finely dispersed sand, whose grains are of an angular shape and have numerous defects, on the one hand, accelerates glass formation and on the other hand, involves certain drawbacks, such as dust formation, stratification, and disturbance of the chemical homogeneity of the batch. Consequently, an efficient method for introducing the finely dispersed sand into a glass batch is its granulation.

TABLE 2

Soda	Mass content, %		
	Na_2CO_3	Na_2SO_4	NaCl
Natural*	74.47	18.70	0.44
Synthesized	99.01	0.02	0.37

* Natural soda also contains 5.10% SiO_2, 0.54% Al_2O_3, 0.11% Fe_2O_3, and the rest is moisture and organic compounds.

Sand is a nonplastic material and its granulation is possible only through using a placticizing additive or an efficient binder. In our research the crystal-hydrate binder was soda and the plasticizer was kaolin, which is a powder with particles of size below 0.05 mm. Furthermore, kaolin may serve as a source of Al_2O_3 in the glass composition. Soda used as the crystal-hydrate binder develops close contacts with the high-melting batch components in granulation, which increases the rate of silica and glass formation [2]. The compositions of working mixtures for making a granulated material concentrate were selected on the basis of industrial glass batches for the purpose of replacing as much as possible the traditional materials with a minimum possible correction of the batch compositions, considering as well the molding properties of mixtures and the granule size of the concentrate, which should not exceed the maximum admissible size of the coarsest batch component, which is sand.

Raw concentrates were granulated by pelletizing and continuous pressing. Pelletizing granulation was implemented on a dish granulator with a dish diameter of 0.4 m, its angle 47°, and its rotational speed 48 min^{-1}. The optimum content of working moisture for pelletizing was determined experimentally. After the end of pelletizing the granules were screened into fractions, and then their moisture content and strength were determined. The results of experiments on the granulation of raw concentrates of different compositions are given in Table 3. Granulation proceeded satisfactorily in all the cases. However, the maximum yield of granules of sizes less than 1 mm did not exceed 20%.

The material concentrates were compressed on a roller press of semi-industrial type with a roller diameter of 120 mm, rotational speed of 20 min^{-1}, clearance between rolls in the compression zones 0.5 mm, the molding pressure 10 MPa, and moisture of the material mixture 5 – 7%. The working mixtures based on sand, kaolin, and soda were prepared in a blade mixer. The feed of the components had the following sequence: sand, water, soda, and kaolin. The total mixing duration was 2 min.

The working mixture prepared in this way was supplied to the roll press hopper. The final product contained 50 – 55% particles (pellets) of size below 0.5 mm and

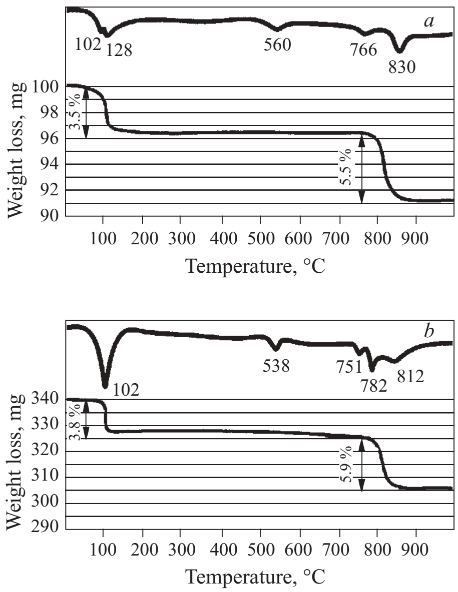

Fig. 1. Derivatograms of batches based on traditional materials (*a*) and granulated concentrates (*b*).

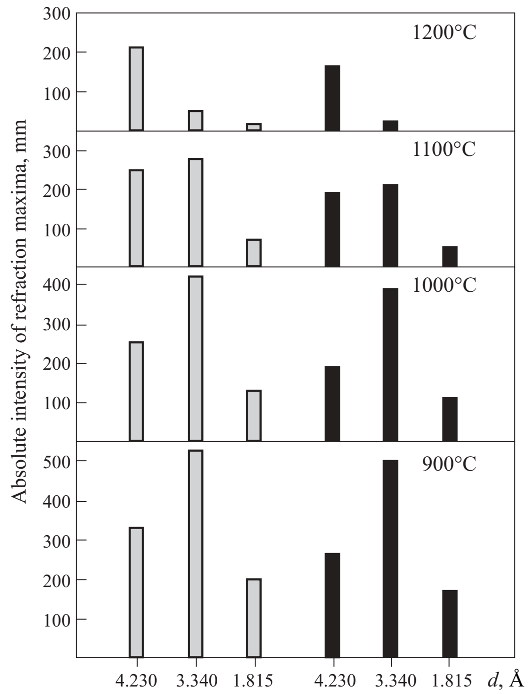

Fig. 2. Histograms of x-ray diffraction maxima of quartz (d = 4.230, 3.340, and 1.815 Å) in container-glass batches: ( ) batch PB-1; ( ) batch PB-2.

40 – 45% irregular plates of size less than 0.5 × 10 × 15 mm, and the quantity of spill did not exceed 5%. The large particles (plates) were additionally crushed in the disintegrator. The total yield of the standard product in the form of pellets of size below 0.5 mm and strength 8 – 10 Pa was at a level of 90 – 95%.

The concentrates obtained by pressing had sufficiently high chemical homogeneity: the deviation in the content of Na_2CO_3 was ± 0.4 %.

The chemical activity of industrial batches for container glass based on traditional raw materials and batches partially or fully replaced by granulated concentrates of substandard materials at the stage of silicate formation was studied using the DTA method in a temperature interval of 200 – 1000°C. It was found that in using granulated concentrates in glass melting, the endothermic effects corresponding to the beginning of the silicate-formation reactions are shifted by 20 – 25°C toward lower temperatures (Fig. 1).

The activity of batches at the stage of glass formation was evaluated using the x-ray phase analysis of glass samples in the course of comparative laboratory melting. The rate of the glass formation process was determined based on the variation of the intensity of the reflection maxima corresponding to quartz. Analysis of the obtained results demonstrated that the intensity of the quartz reflection maxima in batches of container glass with granulated material concentrates (PB-2) within a temperature interval of 900 – 1000°C is lower than in the batch based on traditional material (PB-1). At a temperature of 1200°C the peak corresponding to the interplanar distance of 1.815 Å is absent from the pattern of batch PB-2 (Fig. 2).

Thus, the dissolution of quartz grains proceeds faster in the batch with a granulated concentrate. The increase in the chemical activity of batches in melting is presumably caused by the finely dispersed and defective structure of the material, as well as by the close contact of high-melting components with soda.

Experimental-industrial meltings were performed at the Tomsk Electric Lamp Works in a furnace heated by natural

TABLE 3

Material concentrate	Moisture of moist granules, %	Compressive strength of granules, gf/granule		Granulation duration, min	Yield, %, of granules, of size	
		moist	after blow-drying		finer than 1 mm	1 – 3 mm
Sand – synthetic soda	24 – 26	190 – 210	240 – 260	15 – 18	19	70
Sand – natural soda	20 – 22	180 – 200	200 – 230	12 – 15	12	80
Sand – synthetic soda – kaolin	27 – 29	190 – 210	500 – 600	12 – 14	17	80
Sand – natural soda – kaolin	23 – 25	190 – 200	1200 – 1400	10 – 12	19	77

gas at a heating rate of 20 K/min. Samples for analysis were taken after each 30 min in the temperature interval of 1000 – 1400°C. The results of the meltings indicated that the batches with material concentrates were fully melted and clarified at 1400°C, whereas samples based on traditional materials were not completely clarified. To assess the properties of the container glass produced, standard samples were prepared and tested for their TCLE and thermal and water resistance. In general these parameters satisfy the requirements of state standards imposed on the quality of container glass.

The laboratory and experimental industrial meltings of glasses corroborate the possibility of using substandard raw materials in the form of material concentrate in the production of container glass.

REFERENCES

1. R. S. Zolotareva, I. G. Gurvits, E. A. Obrezan, and N. V. Ivanova, "Homogeneity of the batch and conditions of glass melting depending on the granular composition of heavy soda," *Steklo Keram.*, No. 9, 5 – 8 (1973).
2. V. G. Kalygin, L. N. Kozlova, and O. S. Chekhov, "Mechanochemical effects in structure formation of a compacted batch," *Steklo Keram.*, No. 8, 13 – 15 (1990).